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APPLICATION FOR UNITED STATES PATENT

LOW EMISSIONS FUEL EMULSION

Applicants: Paul J. Berlowitz  
Robert J. Wittenbrink  
Tapan Chakrabarty

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Phyllis A. Taylor

(Typed or printed name of person mailing paper or fee)

*Phyllis A. Taylor*

(Signature of person mailing paper or fee)

Case No. JJD-0101



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PATENT TRADEMARK OFFICE

## LOW EMISSIONS FUEL EMULSION

### FIELD OF INVENTION

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[0001] The present invention relates to an improved fuel which has reduced particulate matter emission characteristics. More particularly the invention is directed to fuels that are in the form of hydrocarbon-in-water emulsions.

### BACKGROUND OF The INVENTION

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[0002] Hydrocarbon-in-water emulsions have many potential uses, such as in internal combustion engines and as a fuel for heating purposes. Indeed, various studies have suggested that burning hydrocarbon-in-water emulsions has the advantage of lowering the nitrogen oxide emissions normally associated with burning hydrocarbons. Emulsions are believed to reduce nitrogen oxide (NO<sub>x</sub>) emissions by lowering the peak flame temperature during their combustion. A lower flame temperature, however, often is associated with an increase in the emission of particulate matter (Pm). This phenomenon, known as the Pm-NO<sub>x</sub> trade off, is believed to limit the improvements one can make to diesel emissions.

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[0003] In recent years there has been a tendency for more stringent emission regulations, including particulate emissions. Therefore, an object of the present invention is to develop a method of more effectively controlling particulate emissions without adversely impacting presently achievable reduced nitrogen oxide emission levels demonstrated for emulsified fuels.

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[0004] In the instance of diesel fueled engines, the reduction of particulate emissions is particularly important. Consequently, another object of the inven-

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tion is to provide an improved diesel fuel having reduced particulate matter emission characteristics.

### SUMMARY OF INVENTION

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[0005] In accordance with the invention reduced particulate matter emissions are achieved with an emulsion of a hydrocarbon and water in which the hydrocarbon is a Fischer-Tropsch (FT) derived hydrocarbon fuel or a mixture of a FT fuel and a conventional hydrocarbon fuel and in which emulsion a major portion of the hydrocarbon has particle sizes of 1 micron or less. Preferably, the emulsion is a hydrocarbon-in-water emulsion.

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[0006] In a particularly preferred embodiment of the invention the hydrocarbon is a FT derived hydrocarbon boiling in the diesel fuel range.

[0007] These and other embodiments will become apparent upon a reading of the detailed description of the invention which follows.

### BRIEF DESCRIPTION OF THE DRAWINGS

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[0008] Figure 1 is a diagrammatic illustration of one arrangement of multiple static mixers used to prepare an emulsion according to the invention.

[0009] Figures 2 and 3 graphically compare the performance of an emulsion of the invention with two non-emulsified fuels in a diesel engine without timing adjustments.

[0010] Figures 4 and 5 graphically compare the performance of the fuels of Figures 2 and 3 with timing adjustment.

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DETAILED DESCRIPTION OF THE INVENTION

[0011] The emulsions of the present invention contain as the hydrocarbon, a Fischer-Tropsch derived hydrocarbon fuel or a mixture of a FT fuel and a conventional hydrocarbon fuel. Preferably, the hydrocarbon is a FT derived fuel.

[0012] As is well known in the art the Fischer-Tropsch process involves the reaction of a hydrogen and carbon monoxide containing feed in the presence of a suitable catalyst to produce a largely normal paraffin synthetic crude. The process is described, for example, in U.S. Patents 5,348,982 and 5,545,674, and suitable catalysts in U.S. Patent 4,568,663, each of which is incorporated herein by reference.

[0013] The hydrocarbon fuels produced in the Fischer-Tropsch process may be separated from the product crude by standard distillation techniques. Additionally, however, the waxy component of the crude may be converted into fuels by known techniques such as hydrotreating, hydroisomerization and hydrocracking. An example of one such process can be found in U.S. 5,378,348, which is incorporated herein by reference.

[0014] In the context of the embodiments of the present invention the Fischer-Tropsch derived hydrocarbon fuel may comprise either the direct liquid product (C<sub>5</sub>+) from the Fischer-Tropsch process, a converted Fischer-Tropsch product, or a blend of the foregoing. Thus, Fischer-Tropsch products boiling in the range of from about 25°C to about 450°C are suitable. Such fuels include that disclosed in U.S. 5,807,413 which patent is incorporated herein by reference. Also included are more convention Fischer-Tropsch products such as those boiling, in the range of about 140°C to about 370°C and preferably in the range of about 160°C to about 350°C.

[0015] The water of the emulsion of the invention may be that typically used in forming fuel emulsions such as tap water, distilled or deionized water. In one embodiment, water from the Fischer-Tropsch process constitutes the continuous phase of the emulsion. Fischer-Tropsch process water typically contains about 5  $\leq 2$  wt% of oxygenates. A typical composition is shown in Table 1 below:

TABLE 1

<u>Oxygenates</u>	<u>Amount</u>
C <sub>1</sub> -C <sub>12</sub> alcohols	0.05 - 2 wt%
C <sub>2</sub> -C <sub>6</sub> acids	0 - 50 wppm
C <sub>2</sub> -C <sub>6</sub> ketones, aldehydes, acetates	0 - 50 wppm
other	0 - 500 wppm

10 [0016] The amount of water used in forming the emulsion may be varied over a wide range. For example, the volume ratio of Fischer-Tropsch hydrocarbon fuel to water may range from about 95:5 to about 60:40.

[0017] The emulsions of the present invention also include a nonionic 15 surfactant or mixture of nonionic surfactants. The type of nonionic surfactants suitable include ethoxylated alcohols, ethoxylated alkyl phenols, ethoxylated carboxylic esters, glycerol esters, sorbital esters and the like. In general, the nonionic surfactant will have an HLB in the range of 5 to 30 and preferably 8 to 15. Among suitable surfactants ethoxylated alkyl phenols having from about 5 20 to about 30 and preferably 10 to 15 mole of ethylene oxide groups deserve special mention.

[0018] The amount of surfactant or mixtures thereof in the emulsion will range from about 0.05 wt% to about 5.0 wt% based on the total weight of 25 hydrocarbons and water with 0.05 wt% to about 2 wt% being typical.

[0019] The emulsion compositions of the invention may include minor but effective amounts of conventional additives such as emulsions stabilizers, antioxidants and the like. In the case where the fuel is diesel fuel the fuel may also contain conventional quantities of diesel fuel additives such as cetane improvers, detergents, heat stabilizers and the like.

[0020] As is known in the art emulsions can be formed by any number of procedures. Central to all of these is providing sufficient shearing of the components to cause emulsification. In the practice of the present invention the fuel is added to a mixture of water and surfactant and sheared under conditions sufficient to produce hydrocarbon particles of predominantly 1 micron in size or less. Stated differently, the particles are substantially uniform in size, i.e., greater than 50% are in the range of about 0.1 to about 1.0 microns in size. Experience has shown that extensive shearing results in the formation of a "gel" and consequently the shearing will be less than that which would produce a gel.

[0021] To achieve the requisite shearing it is particularly preferred to employ one or more static mixtures such as those described in U.S. Patents 5,405,439; 5,236,624; and 4,832,747. In general more than one mixer will be used and the mixers will not be of the same size (length, diameter, number of internal elements). Rather the number, size and elements are selected to adjust mixing efficiency and emulsion particle size. In the practice of the present invention a combination of static mixtures is selected to provide sufficient shearing of the hydrocarbon and water to produce an emulsion having particle sizes predominantly 1 micron or less and less shearing than that which would produce a "gel".

[0022] A diagrammatic illustration of one arrangement of static mixers suitable for carrying out the emulsification of this invention is shown in the accompanying Figure. As shown, each of the six mixers have different dimen-

sions. Obviously, different members and sizes of mixers may be used so long as the requisite shearing is achieved. The dimensions of the illustrated mixers are given in Table 2 below.

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TABLE 2

<u>Mixer</u>	<u>Length, inches</u>	<u>Diameter, inches</u>
1	12	1/2
2	6	1/2
3	4	1/4
4	4	1/4
5	6	3/16
6	4	3/16

[0023] In the arrangement shown in the Figure, a water and surfactant solution is fed to the mixer 1 via line 7 and the Fischer-Tropsch derived hydrocarbon fuel via line 8. The product of each mixer is sequentially fed to the next mixer in the series, e.g., the product of mixer 1 is fed to mixer 2; the product of mixer 2 is fed to mixer 3 and so on. The emulsion exiting mixer 6 via line 9 has a particle size predominantly less than 1 micron. The emulsion in the instance where the Fisher-Tropsch fuel is a diesel fuel, has a viscosity in the range of about 50 to 200 mm<sup>2</sup>/sec at 20°C.

## EXAMPLES

### COMPARATIVE EXAMPLE 1

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[0024] 3000 gms of a non-ionic surfactant (an ethoxylated nonyl phenol having 10 mols of ethylene oxide groups) was added to 9700 gms of water and fed through mixers 1 to 4 shown in the Figure. A Fischer-Tropsch diesel fuel (boiling range ~40°C to 300°C) comprising 90+% of C<sub>6</sub> to C<sub>16</sub> linear paraffins

was also fed with the water and surfactant through the four mixers. The volume ratio of fuel to water was 70:30. The hydrocarbon flow rate was 2650 ml/min and the water surfactant solution flow rate was 1380 ml/min. The temperature was 24°C. The product of mixer 4 was not a hydrocarbon-in-water emulsion.

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#### EXAMPLE 1

[0025] The same ingredients and amounts described in Comparative Example 1 were fed through mixers 1 to 6 shown in the Figure. The flow rate and temperature was the same as in Comparative Example 1. In this instance the product of mixer 6 was hydrocarbon-in-water emulsion having a density of 0.82 gm/cc and a viscosity of 150 mm<sup>2</sup>/sec at 20°C. The hydrocarbon particles averaged 0.7 microns with 95% below 1 micron in size. This emulsion was shelf stable for more than 6 months.

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#### EXAMPLE 2

[0026] The performance of the emulsified Fischer-Tropsch fuel of Example 1 was compared to the same but not emulsified Fischer-Tropsch diesel fuel and to Swedish Class 1 Diesel fuel using a Catapillar 1Y 540 single cylinder heavy duty Research engine. Two conditions were measured, low load (1500 rpm, 60 Nn torque and 3.0 bar BMEP and medium load (1500 rpm, 110 Nm torques and 5.5 bar BMEP.

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[0027] As is known Swedish Class 1 Diesel fuel (also called Urban Diesel ECI) is a standard low emissions reference diesel fuel that produces about 10% to 20% lower NO<sub>x</sub> and 40% to 50% lower particulate matter (Pm) than conventional diesel fuel. The specification for Swedish Class 1 diesel fuel are given in Table 3.

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TABLE 3

Cetane	> 50
Cloud Point	
Summer	0°C
Winter	- 16°C
Density, kg/m <sup>3</sup>	800 - 820
IBP, °C	180
T <sub>95</sub> , °C	285 maximum
Viscosity at 40°C, mm <sup>2</sup> /second	1.2 to 4.0
Sulfur, ppm	10 maximum
Aromatics, vol%	5 maximum
Poly aromatics	not detectable

[0028] The unemulsified Fischer-Tropsch fuel (FTF) has been shown to have excellent emissions performance (see U.S. 5,807,413) with NO<sub>x</sub> reductions of 10-25% and Pm reductions of 40-60% compared with conventional diesel fuels. Figures 2 and 3 show the relative emissions performance of the Fischer-Tropsch fuel and an emulsion of the invention (Example 1) vs. Swedish Class I Diesel fuel at low and medium load.

[0029] As can be seen in Figure 2, the FTF exhibits similar behavior to Swedish Class I Diesel Fuel whereas the a fuel emulsion of the invention shows NO<sub>x</sub> emissions 22% below Swedish Class 1 and Pm 53% below.

[0030] In Figure 3 a fuel emulsion of the invention shows even larger PM reduction (91.5%) than Swedish Class 1 fuel.

[0031] In Figures 4 and 5 the Pm/NO<sub>x</sub> performance of the fuels is plotted against change in spark timing. As can be seen in the case of the FTF and Swedish claim 1 fuels one can retard the timing to lower the NO<sub>x</sub> emissions.